

Investigation of charge transfer and structural distortions during photo-induced excitation of cuprous bis-2,9-dimethyl-1,10-phenanthroline complex by density functional theory

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Abstract

This work reported the investigation of the structural distortions and charge-transfer processes that occurred in the complex of cuprous(I) bis-2,9-dimethyl-1,10-phenanthroline ($\text{Cu}(\text{dmp})_2^+$) upon oxidation to copper(II), $\text{Cu}(\text{dmp})_2^{2+}$, through a excited state of $\text{Cu}(\text{dmp})_2^+$ by density functional theory. The intramolecular electronic transfer from central metal-to-ligand (MLCT) upon the irradiation of light energy is confirmed. Due to this MLCT excitation, the structure of the excited state of $\text{Cu}(\text{dmp})_2^+$ is distorted and reorganized to adapt with the change of charge in central metal. As a result, the excited state of $\text{Cu}(\text{dmp})_2^+$ is formed, which has the similar electronic and structural properties with $\text{Cu}(\text{dmp})_2^{2+}$. The bulky substituents in 2- and 9-positions of the phenanthroline ligands can restrain the structural distort and decrease nonradiative decay rate. Thus, the electronic and steric effects of the ligands in the cuprous photo-sensitive complexes have important consequences in the behavior of their excited state.

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1. Introduction

The investigation of photochemical and photophysical properties of organometallic complexes has been attractive research field [1,2]. Due to the presence of the low-energy π^* orbitals in organic ligands, the complexes usually exhibit strong metal–ligand charge-transfer (CT) adsorption bands in the visible spectrum. Thus they are potentially effective photo-sensitive materials used in the molecular solar energy conversion, molecular sensing, and other optical devices [3–5]. The complex $\text{Ru}(\text{bpy})_3^{2+}$, where bpy is 2,2'-bipyridine is the classic organometallic complex that is used as the photo-sensitive material. It is the most well-studied organometallic complex in history

with the numerous papers being published [6–8]. However, the applications of Ru(II)-based complexes as photo-sensitive materials have been largely limited due to the problem of high costs and environmental pollution. For some other alternatives, such as Re(I) and Os(II)-based complexes, have the same inherent drawbacks. Recently, the Cu(I) coordination complexes are emerging as an attractive alternative [9–12]. From a practical standpoint, solar-energy conversion devices and sensors based on inexpensive copper are more promising than the systems based on the ruthenium or osmium. McMillin and co-workers have established that the Cu(I) complex with 2,9-dimethyl-1,10-phenanthroline ligands (dmp) (Fig. 1(a)), displays an visible excitation with enhanced emission lifetime and has remarkable excited state properties that can be comparable to $\text{Ru}(\text{bpy})_3^{2+}$ [13,14]. Several relating researches have proved that the photo-induced electron transfer (ET) and

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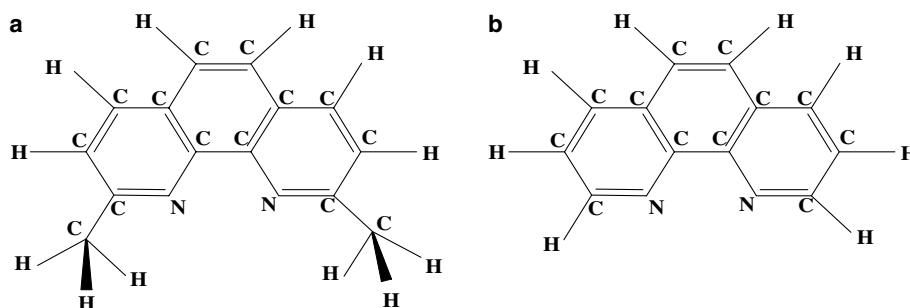


Fig. 1. The skeleton structure of 2,9-dimethyl-1,10-phenanthroline (dmp) and phenanthroline (phen). (a) 2,9-Dimethyl-1,10-phenanthroline and (b) phenanthroline.

charge separation occur during the irradiation of light energy for this complex [15–17]. It is concluded that in order to adapt the electronic density redistribution, this photo-induced electronic movement will cause nuclear movements in the complex, which lead up to distinct variation of structure, or reorganization. Such a structural distortion may have important consequences in limiting the excited state lifetime and determine the steric barrier of the transform from Cu(I) to Cu(II) complexes through an intermediate of excited state in the process of the light energy conversion [18]. Since the complexes with long luminescent lifetimes are usually more useful for energy conversion, we can rationally design and synthesize photo-sensitive materials with high efficiency for solar energy conversion and other potential applications by knowing the nature of the charge separation and its closely related nuclear movement, as well as the influence of the electronic and steric effects of ligands.

The principal purpose of this work is to investigate the structural changes and electronic transfer processes that occur in the complex of cuprous(I) bis-2,9-dimethyl-1,10-phenanthroline ($\text{Cu}(\text{dmp})_2^+$) upon oxidation to copper(II), $\text{Cu}(\text{dmp})_2^{2+}$, through a MLCT excited state of $\text{Cu}(\text{dmp})_2^+$. The stable geometries of $\text{Cu}(\text{dmp})_2^+$, $\text{Cu}(\text{dmp})_2^{2+}$, and the excited states of $\text{Cu}(\text{dmp})_2^+$, are calculated by optimizing the total energy to the minimum using the density functional theory (DFT). The charge transfer direction and degree during excitation are discussed on the basis of analyzing the Mulliken populations of the complex $\text{Cu}(\text{dmp})_2^+$ both in ground state and excited state. The geometrical distortions caused by the charge transfer and the steric and electronic effect of substituents in the 2- and 9-positions of the ligands are investigated by comparing the cuprous complexes with the different ligands.

2. Computational details

All calculations in this investigation have been performed using density functional theory by using GAUSSIAN98 (G98) and Amsterdam density functional program package (ADF2000) [19,20]. In the case of G98, a mixture of Hartree–Fock and DFT along with a Becke three-

parameter hybrid function of Lee, Yang and Parr (B3LYP) was used as the exchange and correlation potential function [21]. The standard LANL2DZ basis sets were applied to all atoms [22]. In the case of ADF2000, the Perdew and Wang's 1991 exchange and correlation function (PW91XC) was used at the generalized gradient approximation (GGA) [23]. The relativistic terms were calibrated by a combined scalar relativistic zero-order regular approximation (ZORA) [24]. The basis sets of triple-zeta Slater Type Orbitals (STOs) with polarization functions were applied to the valence electrons of all atoms (ZORA/TZP). The inner electrons within the atomic shells (i.e., 1s for C and N, 2p for Cu) were handled as a frozen-core approximation. The geometrical and electronic properties of excited states were obtained using orbital occupations method by controlling the assignment of spin- α and spin- β electrons to molecular orbitals. The net spin-polarization of the system was specified to be two. The unrestricted mode was used, which is equivalent with, in ab initio terminology, Unrestricted-Hartree-Fock (UHF) [25]. The bond lengths and angles of the two 2,9-dimethyl-1,10-phenanthroline ligands were fixed during optimization. The pictures of the molecular orbitals and optimized structures were illustrated using a MOLEKEL4.1 molecular visualization program [26].

3. Results and discussion

When $\text{Cu}(\text{dmp})_2^+$ adsorbs the light energy, the electrons may be transferred to the higher energy orbital and the complex stays at the corresponding excited state temporarily. In order to understand the varieties of electronic density distribution during the excitation, the Mulliken charge of $\text{Cu}(\text{dmp})_2^+$ in ground and excited states were calculated in this work. The Mulliken charges of the complex in the stable ground state were obtained by ADF2000 program. For the values of $\text{Cu}(\text{dmp})_2^+$ in the lowest excited state, it was calculated by promoting one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) with the opposite spin using orbital occupations method of ADF2000 program. The results were listed in Table 1. It is observed that the distribution of electronic density is differ-

Table 1
Mulliken charges of the complexes $\text{Cu}(\text{NN})_2^+$, $\text{Cu}(\text{NN})_2^{2+}$, and the excited state of $\text{Cu}(\text{L})_2^+$, (NN = dmp, phen)

	$\text{Cu}(\text{dmp})_2^+$	$\text{Cu}(\text{dmp})_2^+$ -excited state	$\text{Cu}(\text{dmp})_2^{2+}$
Cu	0.251	0.422	0.435
dmp 1	0.375	0.297	0.803
dmp 2	0.375	0.281	0.761
	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{phen})_2^+$ -excited state	$\text{Cu}(\text{phen})_2^{2+}$
Cu	0.360	0.553	0.574
phen 1	0.324	0.177	0.721
phen 2	0.316	0.270	0.705

ent in the ground and excited states of $\text{Cu}(\text{dmp})_2^+$. From the ground state to excited state, the metal loses about 0.17e, while one of dmp ligands gains about 0.09e, and the other gains about 0.08e. It confirms that during the excitation the electrons transfer from central metal copper to dmp ligands (MLCT transfer). It is also noticed that each dmp ligand accepts about half numbers of electrons that flow out from the metal. That is, the electrons move away from the central metal and are assigned to the two dmp ligands equally. To understand this transferring well, we also listed in Table 1 the values of Mulliken charges of the cuprous complex with diimines ligands, $\text{Cu}(\text{phen})_2^+$ (phen = phenanthroline, Fig. 1(b)), which was calculated by the same method [27]. As for this complex during the transfer from the ground state to excited state, the metal loses about 0.19e, and one of phen ligands gains about 0.14e, and the other one gains about 0.05e. Obviously, the electrons are transferred to the two phen ligands in an asymmetric manner. Most of electrons are assigned to only one ligand. Thus the substituents in 2- and 9-positions influence the electronic density redistribution during the process of the excitation obviously.

The same calculation was performed for the Cu(II) complex, $\text{Cu}(\text{dmp})_2^{2+}$, and the data were listed in Table 1 also. The Mulliken charge of central metal is 0.44 in $\text{Cu}(\text{dmp})_2^{2+}$, while it is 0.25 in $\text{Cu}(\text{dmp})_2^+$, and 0.42 in the excited state of $\text{Cu}(\text{dmp})_2^+$. Clearly, a similarity of the net charge in the central metal between copper(I) excited state and copper(II) ground state can be found. Thus, the excited state of $\text{Cu}(\text{dmp})_2^+$ can be viewed as a copper(II)-like species [$\text{Cu}^{2+}(\text{dmp})_2$] $^+$, which is forming through a charge transfer from the central metal to dmp ligands.

The orbital composition of $\text{Cu}(\text{dmp})_2^+$ in stable state were analyzed based on the Mulliken population with the purpose to well understand the nature of electronic transfer during the change from ground state to excited state of the

complex $\text{Cu}(\text{dmp})_2^+$. The data of several selected orbitals were listed in Table 2. The five highest energy occupied orbitals (HOMOs) are made up of five d-orbitals with a slight mixing of the ligands, and the energy levels of these five d-orbitals are split due to the effect of ligand field. The sets of lowest energy unoccupied orbitals (LUMOs) are all made up of the ligands, but each orbital has different assembly of ligands. Fig. 2 illustrated the pictures of the HOMO and LUMO for the complex $\text{Cu}(\text{dmp})_2^+$. It is seen clearly that the HOMO are mainly made up of d-orbitals of metal mixing with a small parts of the N-2p orbital of the ligands. The LUMO is symmetric orbital, which made up of π -orbital combining equally by two dmp ligands. It indicates that the low-lying excitations are originated from the transfer of electrons from d-orbitals of copper to the π^* orbitals of dmp ligands.

The optimized structure of $\text{Cu}(\text{dmp})_2^+$ in ground state was obtained by minimizing the total energy using ADF2000 and GAUSSIAN98 programs, respectively. Several selected bond lengths and bond angles were listed in Table 3 together with the experimental values [28]. The consistent geometries have been yielded by two methods. The stereoview of $\text{Cu}(\text{dmp})_2^+$ was depicted in Fig. 3(a). The coordination geometry around copper cation is best described as a four-coordinated structure and the symmetry of molecular fragment that consists of central metal and four N atoms of the ligands is almost perfectly Td. The structure of

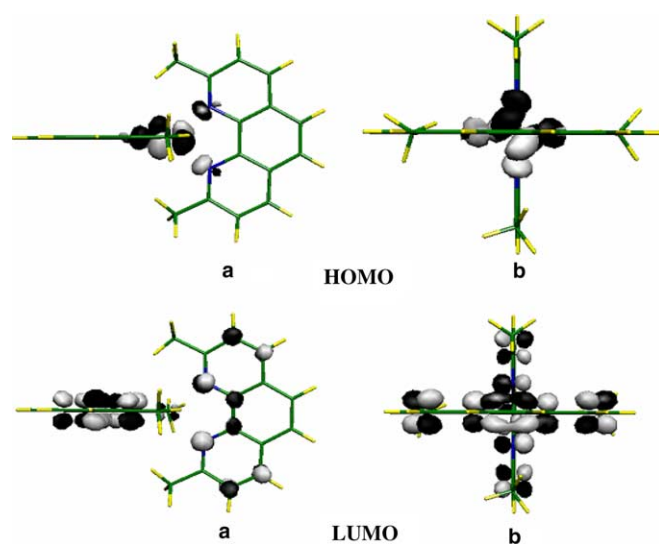


Fig. 2. The profiles of HOMO and LUMO orbitals of $\text{Cu}(\text{dmp})_2^+$. (a and b display the pictures viewed from the different directions).

Table 2
Compositions (%) and energies (eV) of several selected orbitals in $\text{Cu}(\text{dmp})_2^+$

Orbital	83	84	85	86	87(HOMO)	88(LUMO)	89	90	91
Energy (eV)	-8.06	-7.87	-7.62	-7.16	-7.10	-5.36	-5.35	-5.16	-5.14
Cu (d-orbital)	92.6	90.4	87.5	79.5	79.2	3.9	3.8	0	0
dmp1	0	0	2.4	6.0	5.4	45.2	92.8	20.4	72.0
dmp2	0	0	0	2.1	5.8	46.3	0	72.1	19.7

Table 3
Selected bond lengths and angles of the complexes $\text{Cu}(\text{dmp})_2^+$, $\text{Cu}(\text{dmp})_2^{2+}$, and the excited state of $\text{Cu}(\text{dmp})_2^+$

Method:	Complex								
	$\text{Cu}(\text{dmp})_2^+$			$\text{Cu}(\text{dmp})_2^{2+}$			$\text{Cu}(\text{dmp})_2^+$ -excited		
	G98	ADF	Expt. [28]	G98	ADF	Expt. [29]	G98	ADF	
Cu–N1 ^a	2.09	2.04	2.02	2.08	2.04	2.04	2.08	2.03	
Cu–N2	2.09	2.05	2.05	2.08	2.04	2.04	2.10	2.06	
Cu–N3	2.08	2.05	2.06	2.06	2.02	2.06	2.10	2.07	
Cu–N4	2.09	2.06	2.08	2.07	2.05	2.05	2.15	2.14	
N1–Cu–N2	82.2	83.9	81.3	83.6	85.3	84.8	81.6	82.0	
N2–Cu–N3	124.4	120.1	127.0	113.9	110.8	109.1	113.0	107.0	
N3–Cu–N4	82.1	83.8	81.7	84.1	85.4	84.8	80.3	81.0	
N4–Cu–N1	124.4	125.1	126.9	112.5	113.3	117.2	110.2	110.0	
Torsional(dmp1–dmp2)	89.5	88.4	82.0	69.3	71.2	71.4	68.1	67.0	

^a The N1, N2, N3, N4 denote the different nitrogen atom of the dmp ligands (see Fig. 3).

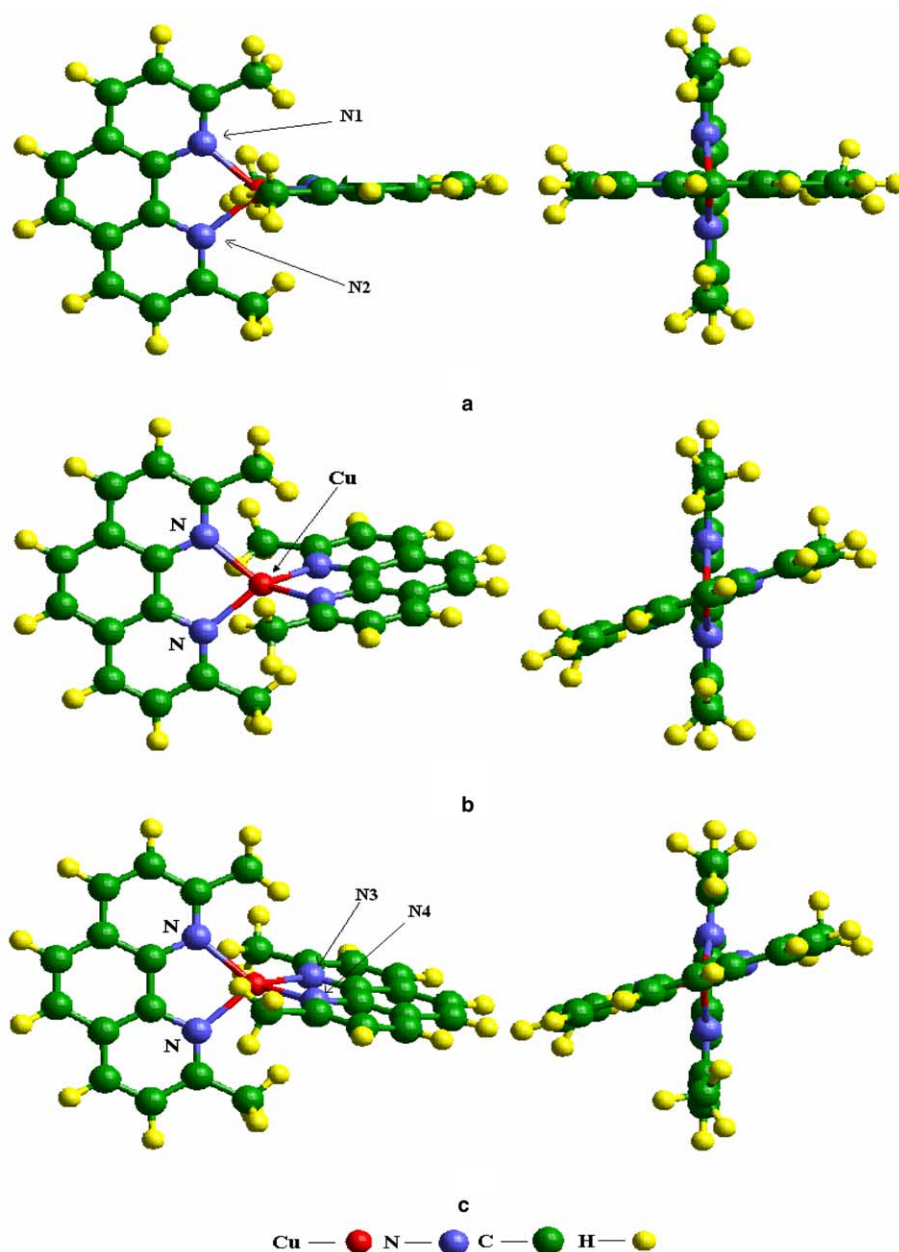


Fig. 3. The optimized structures of cuprous bis-2,9-dimethyl-1,10-phenanthroline complexes viewed from different directions for both (a) $\text{Cu}(\text{dmp})_2^+$ and (b) $\text{Cu}(\text{dmp})_2^{2+}$ in ground state, and (c) $\text{Cu}(\text{dmp})_2^+$ in excited state.

corresponding Cu(II) complex, $\text{Cu}(\text{dmp})_2^{2+}$, was also optimized using the same computational conditions and the optimized results along with the experimental values [29] were listed in Table 3. The geometrical figure of $\text{Cu}(\text{dmp})_2^{2+}$ was shown in Fig. 3(b). Obviously, the geometrical structures of these two cuprous complexes largely depend on the charge of central copper. It is found that although there is no change in coordination number, there are substantial structural differences between the steric geometries of $\text{Cu}(\text{dmp})_2^+$ and $\text{Cu}(\text{dmp})_2^{2+}$. The distances between copper and dmp ligands in two complexes are not changed so much (Table 3), whereas there are large variations for the relative directions of two dmp ligands. By losing one electron from Cu(I) to become Cu(II) complex, the angles between two ligands decrease from a values of 88.4° to 71.2° . From a ideal tetrahedral structure of $\text{Cu}(\text{dmp})_2^+$, the structures is flattened to form a distortion tetrahedral of $\text{Cu}(\text{dmp})_2^{2+}$. It matches with the coordination rule of cuprous complexes [30]. The electronic configuration of Cu(I) is d^{10} and it generally prefers to be four-coordinate with a tetrahedral geometry, while Cu(II) is d^9 and it adopts a Jahn-Teller distorted geometry that is usually 5- or 6-coordinate [30]. The two dmp ligands in Cu(II) complex is flattened in order to adapt the increasing coordinate sites. However, the bulky methyl substituents in the 2- and 9-positions limit large flattening distortion. Thus, it is reasonable that the $\text{Cu}(\text{dmp})_2^{2+}$ does not exhibit planar structure but the intermediate between the ideal tetrahedral and planar structure.

The optimization of the first excited state was performed with a model by promoting one electron from the HOMO to LUMO with the opposite spin using orbital occupations method of ADF2000 program. The structure shown in Fig. 3(c) indicates that a significant rotation of the dmp ligands is expected in the lowest energy excited state of $\text{Cu}(\text{dmp})_2^+$ during the excitation. With a change from ground state to excited state of $\text{Cu}(\text{dmp})_2^+$, the angles between two dmp ligands decrease from a values of 88.4° to 67.0° (Table 3). The excited state of $\text{Cu}(\text{dmp})_2^+$ displays a distorted tetrahedral geometry, which is very similar to that of $\text{Cu}(\text{dmp})_2^{2+}$. Thus, the ground state structure of $\text{Cu}(\text{dmp})_2^{2+}$ provides a reasonable description of the MLCT excited state of $\text{Cu}(\text{dmp})_2^+$. It is acceptable because the electron transfers from central metal to dmp ligands during the change from ground state to excited state of $\text{Cu}(\text{dmp})_2^+$. Such electronic transfer makes the central metal in the excited state of $\text{Cu}(\text{dmp})_2^+$ having the charge value similar with that of $\text{Cu}(\text{dmp})_2^{2+}$. Therefore, the distortion occurs during the excitation process of $\text{Cu}(\text{dmp})_2^+$ to form a excited state structure similar with Cu(II) complex. The total energy of the excited state $\text{Cu}(\text{dmp})_2^+$ (-370.75 eV) is more closer to that of $\text{Cu}(\text{dmp})_2^{2+}$ (-371.09 eV) than $\text{Cu}(\text{dmp})_2^+$ itself (-373.12 eV). Therefore in the energy viewpoint, the structural variation during the excitation shows a potential ability of evolution from Cu(I) to Cu(II) complex by an intermediate of excited state. The absorbed light energy provides a driving force for the

reaction of $\text{Cu}(\text{dmp})_2^+$ to $\text{Cu}(\text{dmp})_2^{2+}$. An obvious result can be derived if we compare the distortion occurred in the excitation process of $\text{Cu}(\text{dmp})_2^+$ with that of the complex $\text{Cu}(\text{phen})_2^+$ (Table 4). The $\text{Cu}(\text{dmp})_2^+$ has relative small structural distortion during the excitation than that of $\text{Cu}(\text{phen})_2^+$ (Figs. 3 and 4). That is, the bulky substituents in 2- and 9-positions can restrain the structural distort, which occurs when the positive charge of central metal is increased. Usually, the structural distortion may lead to fast nonradiative decay from the excited state and limit the excited state lifetime [18]. Thus the present work demonstrates that the bulky substituents in the 2- and 9-positions are able

Table 4
Selected bond lengths and angles of the complexes $\text{Cu}(\text{phen})_2^+$, $\text{Cu}(\text{phen})_2^{2+}$, and the excited state of $\text{Cu}(\text{phen})_2^+$

	Complex			Expt. [18]
	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{phen})_2^+$ -excited state	$\text{Cu}(\text{phen})_2^{2+}$	
Cu–N1 ^a	2.03	2.00	2.04	2.02
Cu–N2	2.04	2.02	2.04	2.04
Cu–N3	2.03	2.00	2.04	2.02
Cu–N4	2.07	2.04	2.07	2.05
N1–Cu–N2	85.9	87.2	85.7	81.7
N2–Cu–N3	126.4	101.1	101.7	128.4
N3–Cu–N4	85.0	86.8	84.9	82.2
N4–Cu–N1	120.9	99.6	96.7	122.9
Torsional (phen1–phen2)	92.1	43.7	35.5	

^a The N1, N2, N3, N4 denote the different nitrogen atom of the dmp ligands (see Fig. 3).

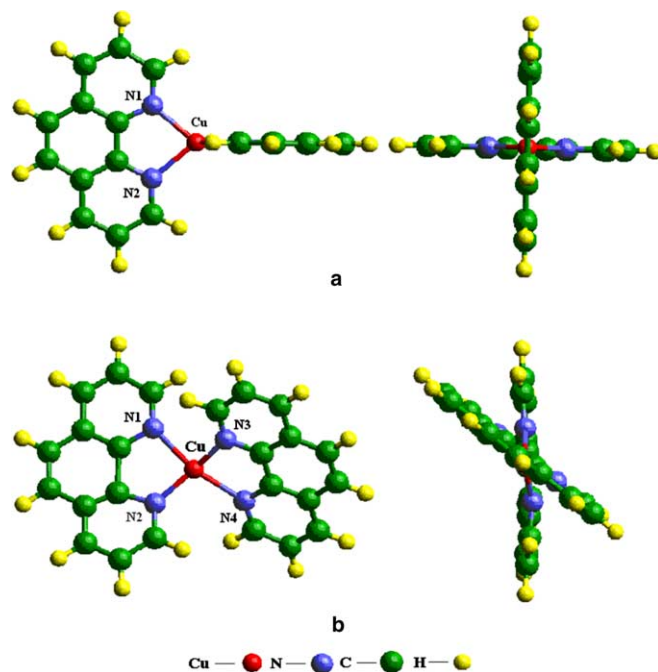


Fig. 4. The optimized structure of $\text{Cu}(\text{phen})_2^+$: (a) in ground state and (b) in the lowest excited state.

to decrease nonradiative decay rate and then increase the excited state lifetime.

4. Conclusions

In this work, the properties of electronic transfer excitation and structural distortion of $\text{Cu}(\text{dmp})_2^+$ have been investigated. Our results confirm that the shapes of stable geometries of cuprous complexes depend on the charge values of central copper largely. It varies from an ideal tetrahedral structure of Cu(I) complex to a distorted tetrahedral of Cu(II) complex. It is observed that after the complex $\text{Cu}(\text{dmp})_2^+$ captured the light energy, the electronic density is redistributed by a way of MLCT excitation (electron transfer from metal to the ligands). The structural distortion of the excited state of $\text{Cu}(\text{dmp})_2^+$ occurs because of the varieties of central metal charge caused by the electronic transfer. Such structural distortion determines the lifetime of excited state, which is an important character as effective photo-sensitive materials. The MLCT excited state of $\text{Cu}(\text{dmp})_2^+$ exhibited behaviors consistent with $\text{Cu}(\text{dmp})_2^{2+}$. The similarity of the structure and energy between $\text{Cu}(\text{dmp})_2^{2+}$ and the excited state of $\text{Cu}(\text{dmp})_2^+$ shows a potential ability of the evolution from Cu(I) to Cu(II) complexes through a intermediate of excited state. By comparing the structural varieties during the excitation of $\text{Cu}(\text{dmp})_2^+$ and $\text{Cu}(\text{phen})_2^+$, our results demonstrate that the bulky substituents in 2- and 9-positions can restrain the structural distortion. It is concluded that the bulky substituents in 2- and 9-positions is able to decrease nonradiative decay rate and then improve the excited state properties. Therefore, the electronic and steric effects of the ligands in the cuprous photo-sensitive complexes have important consequences in their inner structural reorganization and influence the efficiency of the solar energy conversion.

References

- [1] N.J. Turro, *Modern Molecular Photochemistry*, University Science Books, Mill Valley, CA, 1991.

- [2] D.M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum Press, New York, 1994.
- [3] C.A. Mirkin, M.A. Ratner, *Annu. Rev. Phys. Chem.* 43 (1992) 719.
- [4] V. Sobolev, S. Lemehov, N. Messaoudi, P.V. Uffelen, H.A. Abderahim, *J. Nucl. Mater.* 319 (2003) 131.
- [5] J. Solis-Rodarte, H. Fu, K.N. Ivanov, Y. Matsui, A. Hotta, *Ann. Nucl. Energy* 29 (2002) 585.
- [6] P.Y. Chen, T.J. Meyer, *Chem. Rev.* 98 (1998) 1439.
- [7] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A.V. Zelewsky, *Coord. Chem. Rev.* 84 (1988) 85.
- [8] B.O. Regan, M. Gratzel, *Nature* 353 (1991) 737.
- [9] D.V. Scaltrito, D.W. Thompson, J.A.O. Callaghan, G.J. Meyer, *Coord. Chem. Rev.* 208 (2000) 243–266.
- [10] O. Horvath, *Coord. Chem. Rev.* 135 (1994) 304.
- [11] R.M. Everly, D.R. McMillin, *J. Phys. Chem.* 95 (1991) 9071.
- [12] D.R. Crane, P.C. Ford, *J. Am. Chem. Soc.* 113 (1991) 8510.
- [13] M.W. Blaskie, D.R. Mcmillin, *Inorg. Chem.* 19 (1980) 3519.
- [14] D.R. Mcmillin, J.R. Kirchoff, K.V. Goodwin, *Coord. Chem. Rev.* 64 (1985) 83.
- [15] C. Kotal, *Coord. Chem. Rev.* 99 (1990) 213.
- [16] O. Horvath, *Coord. Chem. Rev.* 135 (1994) 303.
- [17] M. Ruthkosky, C.A. Kelly, F.N. Castellano, G.J. Meyer, *Coord. Chem. Rev.* 171 (1998) 309.
- [18] N.H. Damrauer, T.R. Boussie, M. Devenney, J.K. McCusker, *J. Am. Chem. Soc.* 119 (1997) 8253.
- [19] R.M. Dreizler, E.K.U. Gross, *Density Functional Theory, An Approach to the Quantum Many-Body Problem*, Springer, Berlin, 1990.
- [20] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *J. Comput. Chem.* 22 (2001) 931.
- [21] W.C. Ermler, Y.S. Lee, K.S. Pitzer, *J. Chem. Phys.* 70 (1979) 293.
- [22] F.C. Guerra, J.G. Snijders, B. Velde, E.J. Baerends, *Theor. Chem. Acc.* 99 (1998) 391.
- [23] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, *Phys. Rev. A* 46 (1992) 6671.
- [24] E.V. Lenthe, A.E. Ehlers, E.J. Baerends, *J. Chem. Phys.* 110 (1999) 8943.
- [25] T. Ziegler, A. Rauk, E.J. Baerends, *Theoret. Chim. Acta* 43 (1977) 261.
- [26] S. Portmann, H.P. Luthi, *Chimia* 54 (2000) 766.
- [27] X.J. Wang, C. Lv, M. Koyama, M. Kubo, A. Miyamoto, *J. Organomet. Chem.* 690 (2004) 187.
- [28] G. Dessy, V. Fares, *Cryst. Struct. Commun.* 8 (1979) 507.
- [29] M. van Meerssche, G. Germain, J.P. Declercq, L. Wilputte-Steinert, *Cryst. Struct. Comm.* 10 (1981) 47.
- [30] P.J. Burke, D.R. McMillin, W.R. Robinson, *Inorg. Chem.* 19 (1980) 1211.